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INDUSTRIAL REJECTION: REMOVAL OF HEAVY METALS BASED ON CHEMICAL PRECIPITATION AND RESEARCH FOR RECOVERABLE MATERIAL IN BYPRODUCTS

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Abstract:

With the acceleration of urbanization and the rapid development of industry and agriculture, a large number of industrial wastewater containing heavy metal is produced. In this study we worked on industrial rejection.

The method for removing heavy metals from industrial wastewater based on chemical precipitation method is proposed in this paper, which utilizes lime (CaO), limestone (CaCO₃), and sodium hydroxide (NaOH). Research on gypsum (CaSO₄, 2H₂O) in byproducts resulted from precipitation is carried out based on thermal analyses, infrared spectra and XRD examinations.

The characterization of the effluent showed that's very hard, rich in sulphate, chlorides, orthophosphate and in heavy metals. The results show that the examined chemical coagulants were all efficient in the removal of the studied metals (Cu, Cd, Fe, Co and Zn).

The overall results indicate that the optimum pH for hydroxide precipitation of the studied metals is varied between pH 6.0 and 10.0. Since all effluent guidelines require an effluent pH between 7 and 8, the use of carbonate treatment is, therefore, recommended because its buffering capacity value is around pH 7. The analyzes carried out on the byproducts of treatment (FTIR, XRD, TGA/TDA) show that they are mostly composed of gypsum: calcium sulphate dihydrate (CaSO₄·2H₂O).

Keywords: Industrial Wastewater; Heavy Metals; Chemical Precipitation; Removal; Treatment Product.

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1. Introduction

In the last few decades, water pollution has become a significant global problem due to the rapidly growing population and industrialization. Actually, water pollution by chemicals has become a

major source of concern and a priority for both society and public authorities, but more importantly, for the whole industrial world.

The present study was to investigate the removal efficiency of heavy metals and to research to gypsum respectively from waste discharged from industrial rejection.

Unlike organic contaminants, most of the heavy metals do not undergo microbial or chemical degradation. The heavy metal-contaminated sites cause threats and hazards to humans and the ecosystem by direct contact with contaminated soil; through the food chain (soil–plant–human); and by contaminating the ground and surface water resources [1, 2, 3]. During the last three decades, several physical, chemical and biological technologies have been reported such as chemical precipitation, coagulation/flocculation, electrochemical treatment, adsorption, ion exchange and membrane filtration have been employed [4, 5, 6, 7, 8, 9, 10, 11]. Of these methods, chemical precipitation is most widely practiced in industry, mainly for the simplicity of process control, effective over a wide range of temperature and low cost of operation. Based on previously reported research, precipitation can mainly be divided into hydroxide precipitation methods and sulfide precipitation methods [12, 13]. Common hydroxide precipitants include lime (Ca(OH)_2), limestone, sodium hydroxide (NaOH), sodium bicarbonate ($\text{Na(HCO}_3)_2$), sodium sulfide (Na_2S) and sodium hydrosulfide (NaHS), which can release hydroxide ion bound metals to form insoluble hydroxide precipitates [14, 15, 16, 17]. The selection of these chemicals should be able to meet the maximum contaminant level standards or to reach the desired final concentration required for recycling [18, 19, 20, 21]. As legislation for metal discharge to environment becomes more stringent and metal resources become increasingly scarce, heavy metal sludge may need to be recyclable [22].

In the present work, precipitations of heavy metals namely zinc, copper, iron, cadmium and cobalt, from the industrial rejection with lime (calcium hydroxide), limestone (CaCO_3), and sodium hydroxide (NaOH) were investigated. Evaluation and correlation between different chemical precipitants for metal removal are also the aim of this work. Research on gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in byproducts resulted from precipitation is carried out based on thermal analyses, infrared spectra and XRD examinations

2. Materials and Methods

The samples are taken from the collector, which it is a collector bringing to the marine environment the effluents from the industrial unit. The water used in the various production units of this industry is marine water.

2.1. Sampling and Characterization

Wastewater samples were collected from collector at monthly intervals. Samples were collected in polyethylene bottles and transported to the laboratory in a small refrigerator ($\sim 4^\circ\text{C}$). Field pH and conductivity measurements were made by using standard electro chemical techniques. All wastewater samples were analyzed on the same day for sulfates (SO_4^{2-}) and soluble reactive phosphorus (PO_4^{3-}) according to the American standard methods [23].

The concentration of heavy metals (Cd, Cu, Fe, Zn, Co) in the wastewater was determined by atomic absorption spectrometry “Unicam 929 AA). Prior to measurement of the samples, all of the samples were acidified with nitric acid to $\text{pH} < 2$ to dissolve any precipitates.

2.2. Heavy Metal Ion Removal

Figure 1 Illustrates the schematic of experiments and main operations are described as follows.

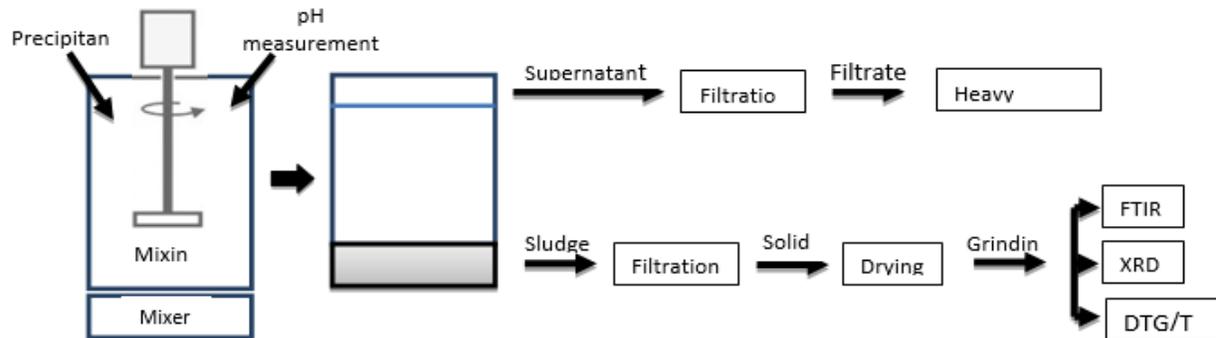


Figure 1: The schematic of experiments

The Jar tests procedure was used in all experiments. Jar tests with a series of five beakers (1L each) were conducted to investigate the effect of precipitant dosages on heavy metal removal at room temperature of 20 ± 2 °C. In each beaker calculated dosages of lime, limestone and NaOH were added into heavy metal solutions during the flash mixing process at the speed 400 rpm for a period of 3min followed by flocculation at the speed of 40 rpm for a period of 20 min. One of these beakers was kept as the control one without adding any chemical treatment. The pH was monitored by PHS-3D digital pH meter calibrated by buffer solutions of known value.

The suspensions settled for 60 min and the supernatants nearly 1 cm below the water surface was collected using a syringe and filtered through $0.45\mu\text{m}$ membranes, acidified by nitric acid and analyzed for heavy metal of each beakers. All measurements of metal concentrations were done in triplicates and the arithmetic mean concentrations of heavy metals were reported.

2.3. Characterization of Precipitation By-Products

The precipitates were dried at 60 °C for 24 h and ground below $30\mu\text{m}$ and then analyzed by Philips X' Pert MPDX-ray powder diffraction apparatus. XRD operating parameters were as follows: wavelength of 1.54 \AA , voltage of 40 kV, current of 200 mA, 2θ scan range of 3° – 80° ,

Thermal analyses were used to identify chemical compounds in precipitates, as some chemical compounds may be amorphous or very poorly crystallized particles, which cannot be detected by XRD. The samples of each precipitates were placed in the rhodium-platinum crucible of 5.8mm diameter and 4mm high. During the examination, the samples were subjected to heating rate of 10 °C/min under flowing nitrogen gas ($80\text{ cm}^3/\text{min}$) in the temperature range of 25 – 1000 °C.

FTIR spectra were collected on a Nicolet Avatar 205 Fourier transform IR spectrophotometer. Samples were mixed with KBr and finely powdered to prepare pellets. The spectra were recorded with 2 cm^{-1} resolution in the range of 4000 – 400 cm^{-1} .

3. Results and Discussions

3.1. Characterization of the Effluent

The physical and chemical characteristics of the industrial wastewater are given in Table 1. The pH of this wastewater was acid and the electric conductivity was slightly high at the range of 79.6 ms/cm. The orthophosphates, sulfates and chlorides were slightly high at the range of 197.5, 15292.8 and 24790 mg/l, respectively. The average background concentration of copper, cadmium, zinc, plumb, cobalt and iron were 0.06, 0.192, 5.88, 0.351, 0.136 and 5.87 mg/l, successively (Table 1).

Table 1: Physical and chemical characteristics and metals concentration of industrial wastewater (from period of 12 months)

Eléments	pH	E.C (ms/cm)	PO ₄ ³⁻ mg/l	SO ₄ ²⁻ (mg/l)	Cd ²⁺ mg/l	Cu ²⁺ mg/l	Fe ²⁺ mg/l	Zn ²⁺ mg/l	Co ²⁺ mg/l	Pb ²⁺ (mg/l)
Mean Value	2.15	79.6	197.5	15292.8	0.192	0.06	5.87	5.88	0.136	0.351
Norme [28]	7- 8	-----	0.07	2710	0.05	0.5	0.01	2	0.0005	0.3

The effluent is charged in various elements, all concentrations exceed the standards of quality of marine waters [24]. It is very hard, rich in sulphate, chlorides, orthophosphate and harmful metallic elements.

3.2. Removal of Heavy Metals

3.2.1. Sodium Hydroxide at Different Ph

By using sodium hydroxide as precipitant, the results obtained (Fig. 2) showed that increasing the pH value increased metals precipitation. The optimum pH for Cu, Cd, Fe and Zn was 7 at which removal increased up to 99%, while Co removed at 84.5%. Increasing the pH value to 9, the removal rate of all metals did not show any further improvement.

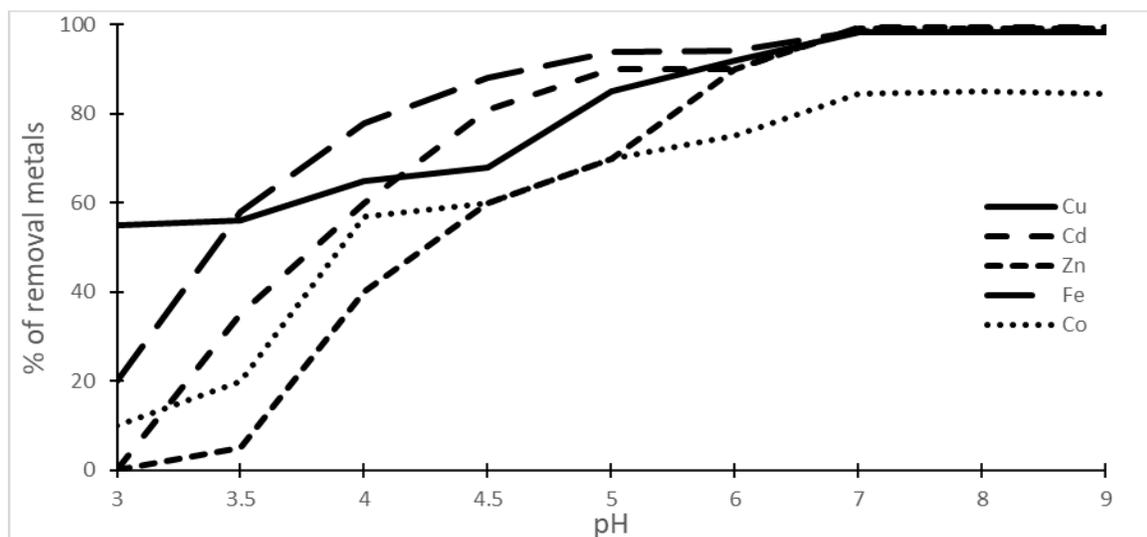


Figure 2: Effect of NaOH at different pH on the precipitation of heavy metals

3.2.2. The Use of Lime at Different Doses

Further study was carried out to investigate the use of lime (CaO). Different doses of lime were added to effluent ranging from 50 to 2000 mg/l. The study covered the range of pH from 3.0 up to 10.0 according to the addition of lime dose to the effluent. Remarkable improvement in the precipitation system was demonstrated by increasing the pH value (Fig. 3). At 1000 mg/l lime the pH reached 7.5 at which over 99% of Cd and Cu each was removed. At this point, 86.7% of Co, 94% of Fe and 75.5% of Zn were removed.

By increasing the pH to 9.0, the removal rate of Cd and Cu reached 100%. However, the optimum removal of Fe and Zn were achieved namely 96% and 89% respectively. The removal rate of Co did not exhibit any further increase and was still at 86.7%.

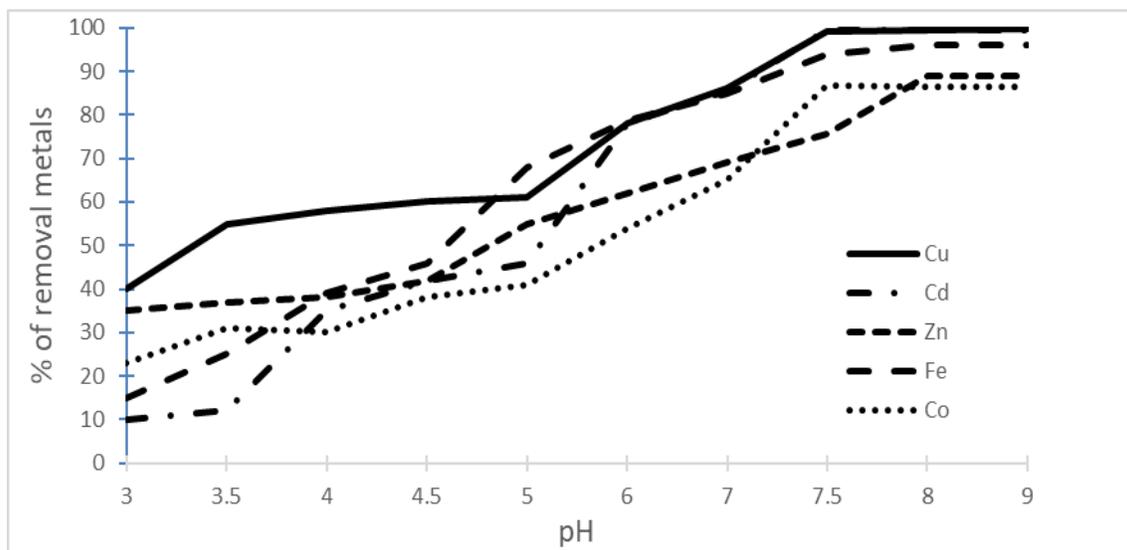


Figure 3: Effect of different lime (CaO) doses on the removal of heavy metals

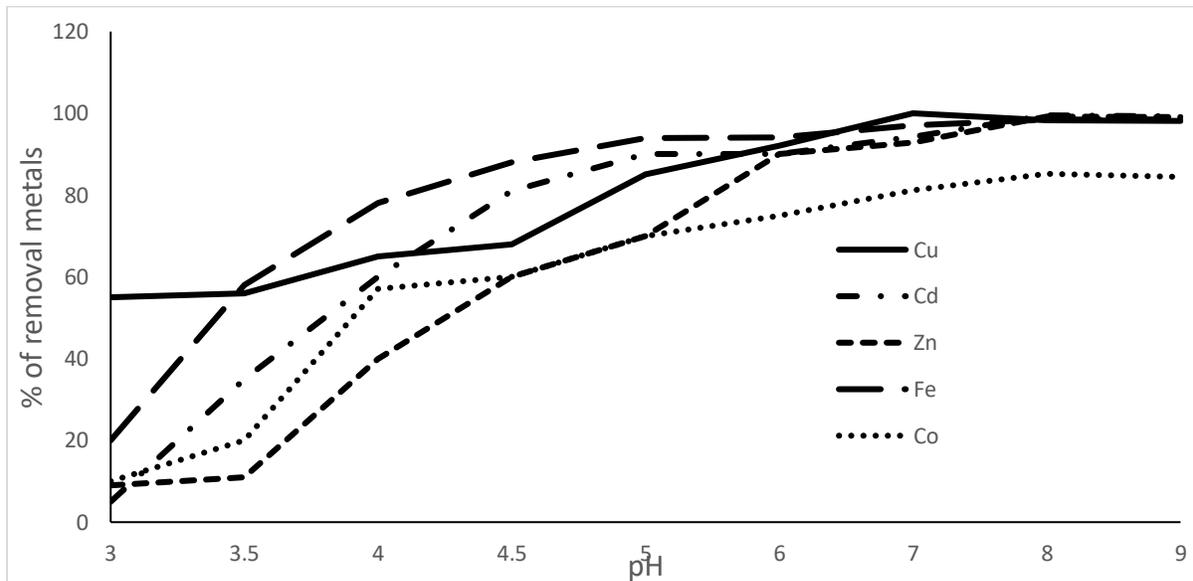
3.2.3. The Use of Limestone at Different Doses

Use of limestone (CaCO₃) at different doses covering the range from 0.2 g/l to 5.0 g/l was investigated. Results obtained (Fig. 4) showed that increasing the CaCO₃ dose from 100 to 1200 mg/l led to a slow increase in the pH value up to 3.5 (Table 2). Further addition of CaCO₃ up to 4.0 g/l exhibited very slow increase of the pH up to 8 which is attributed to carbonate buffering capacity system. The removal rate of the metals studied (Fig. 4) showed that use of 1.2 g/l raised the pH to 3.5 and the removal of Cu, Fe, Co, Zn and Cd to 56, 18, 10, 1.5 and 0.5%, respectively.

By increasing the CaCO₃ to 3.0 g/l, the pH reached 7.0 at which 100% of Cu was achieved. At this point Fe, Cd, Zn and Co removal reached 97, 94.3, 92.9 and 81.1% respectively. One significant benefit of the CaCO₃ is the buffering effect provided by both carbonate and bicarbonate ions. Table 2 records the gradual change in the pH of the wastewater according to the added dose of limestone.

Table 2: Effect of different calcium carbonate (CaCO_3) doses on the pH of the effluent

Limestone (CaCO_3) dose (mg/l)	pH value of the wastewater
0.0	2.15
100	2.3
250	2.45
500	2.85
1000	3.15
1200	3.5
1500	4.75
2000	5.85
3000	7.0
4000	8.0
5000	8.23

Figure 4: Effect of different limestone (CaCO_3) doses on the removal of heavy metals

3.2.4. Limestone in Combination With Lime at Different Doses

In order to neutralize the medium, the CaCO_3 and $\text{Ca}(\text{OH})_2$ reagents were combined, the protocol is as follows: after stirring the effluent for one hour with CaCO_3 and filtration, added different mass of $\text{Ca}(\text{OH})_2$. The medium became almost neutral (pH = 6.21). The test to be retained is that consisting in using 60% of CaCO_3 and 40% of $\text{Ca}(\text{OH})_2$. The results indicate that at this pH (6.21) 90% of Cd, 77% of Co, 93% of Cu, 96% of Fe, and 99% of Zn were removed.

Correlation between the efficiency of the studied chemical coagulants on the removal of Cu, Cd, Fe, Co and Zn at the optimum pH is given in Table 3.

Table 3: Correlation between the efficiency of the studied chemical coagulants on the removal of heavy metals at the optimum pH

Chemical coagulant	Optimum pH	% of metal removal				
		Cu	Fe	Cd	Zn	Co
NaOH	7	97.33	94.05	95.47	94.14	84.55
Lime (CaO)	7.5	99.3	96	99.48	94.5	86.7
Limestone (CaCO ₃)	7	89.06	91	83.6	86.9	79.1
Lime + Limestone	6.21	93	94	90	99	77

This correlation shows that the examined chemical coagulants were all efficient in the removal of the studied metals. Between 86 to 99.4% of Cu, Fe, Cd and Zn could be removed. However, Co was less removed within the range between 77 to 86.7%. The highest efficiency of chemical coagulants was exhibited by lime and NaOH. The limestone also gives good results, but it required high dose between 3000 or 5000 mg/l to reach pH 7.0 and 8.23, respectively. On the other hand, lime exhibited high efficiency of metals removal at pH 7.5 (Table 3). Still, lime removal efficiency at pH 7.5 was 99.3% for Cu, 96% for Fe, 86.7% for Co, 99.48 for Cd and 94.5% for Zn.

It can be concluded that the co-precipitation of metal hydroxides is governed by the concentration of metal ion in solution and the pH value [20, 25, 26, 27]. As the pH increases, the co-precipitation of metal hydroxide increases. The overall results indicate that the optimum pH for hydroxide precipitation of the studied metals is varied between pH 6.0 and 10.0. Since all effluent guidelines require an effluent pH between 7 and 8, the use of carbonate treatment is, therefore, recommended because its buffering capacity value is around pH 7. However, lime (CaO) provides substantial precipitation capacity and an economic mean of treatment for heavy metal removal. The disadvantage is the difficulty to control the pH of the liquid waste. To get over such disadvantage acids and NaOH could be used to control the required pH if needed. The sludge formed could be handled as hazard chemicals since it contains heavy metals. However, the most important is that heavy metals were removed from the wastewater that could be reused safely without any hazard to man.

3.3. Characterization of Precipitation By-Products

The results of characterization of the byproducts, recovered after treatment, by X-ray diffraction (XRD), infrared spectroscopy (IR), and differential thermogravimetric analysis (DTA / ATG) are presented in Figures 5,6 and 7.

3.3.1. TGA-DTA Analyses

Figure 5 shows the TGA–DTA curves of the byproducts of treatment by lime, limestone and neutralization by NaOH. All samples have similar thermal decomposition behaviors. As shown in Fig.6, endothermic effects are recorded at 66°C and 133°C, which should correspond to the evaporation of the adsorbed water and residual organics on the surface of the collected product [28]. The first endothermic effect at around 66°C is attributed to the loss of 1.5 moles of water molecules from the residual dihydrate to pass to the hemihydrate (CaSO₄, 0.5H₂O), which then will end up losing the remaining ½ mole of water at the second very intense endothermic effect around 133°C to pass to anhydrite III (CaSO₄) according to the following reactions:



Effects recorded around 428°C corresponds to the transformation of anhydrite III of hexagonal structure into anhydrite II of orthorhombic structure (eq. 3) [29]:



The total weight losses of the samples in the temperature range up to 800°C were approximately 21%, 22.2% and 27.4% for lime, limestone and neutralization by NaOH. These weight losses should correspond on the removal of water and the decomposition of the carbonate ions in these samples (eq.4)[30]:

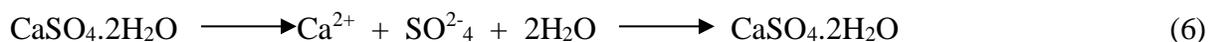


3.4. FTIR

The FTIR spectra of the byproducts of treatment by lime, limestone and neutralization by NaOH are shown in Figure 6. Similarities of these spectra are underlined by the presence of the characteristic's bands of water vibrations as well as the characteristics bands of sulfate vibrations. In the spectrum of the recovered precipitate, the presence of water is characterized by two bands [31, 32]. The broad band at 3300~3700 cm^{-1} is ascribed to the symmetrical and asymmetrical elongation of H_2O ($\nu_1 \text{H}_2\text{O}$) and the adsorbed water molecules and the band at 1600~1700 cm^{-1} is assigned to the water molecules deformation vibrations ($\nu_2 \text{H}_2\text{O}$). Indeed, we noted on the infrared spectrum the presence of very strong absorption around 1117-1150 cm^{-1} and 600 – 668 cm^{-1} . These absorptions correspond to the stretching of sulfate groups $\nu_3 \text{SO}_4^{2-}$ (asymmetric elongation of sulfate) and to the bending modes vibrations of sulfate groups $\delta \text{O-S-O}$ ($\nu_4 \text{SO}_4^{2-}$ asymmetric deformation of sulfate) respectively. These results are in agreement with other studies [33, 34, 35, 36, 37].

3.4.1. Diffraction XRD

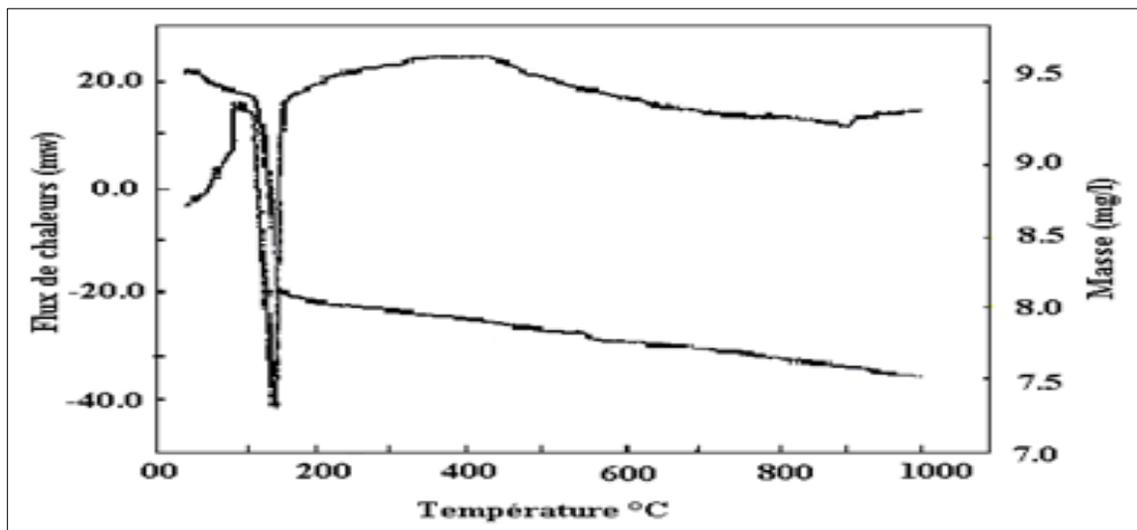
We performed a spectroscopic analysis by X-ray diffraction after treatment with lime, NaOH and calcite. The spectra obtained are shown in Figure 7. Several diffraction lines of this spectrum have been identified as those of $\text{CaSO}_4, 2\text{H}_2\text{O}$ and $\text{CaSO}_4, 0.5\text{H}_2\text{O}$ [38, 39] in the two spectra relating to lime and NaOH (Figure 7a, 7b). On the other hand, in spectrum 7c, relating to the calcite treatment, there are only 3 peaks of the $\text{CaSO}_4, 2\text{H}_2\text{O}$ phase. this can be explained by the following equilibriums:



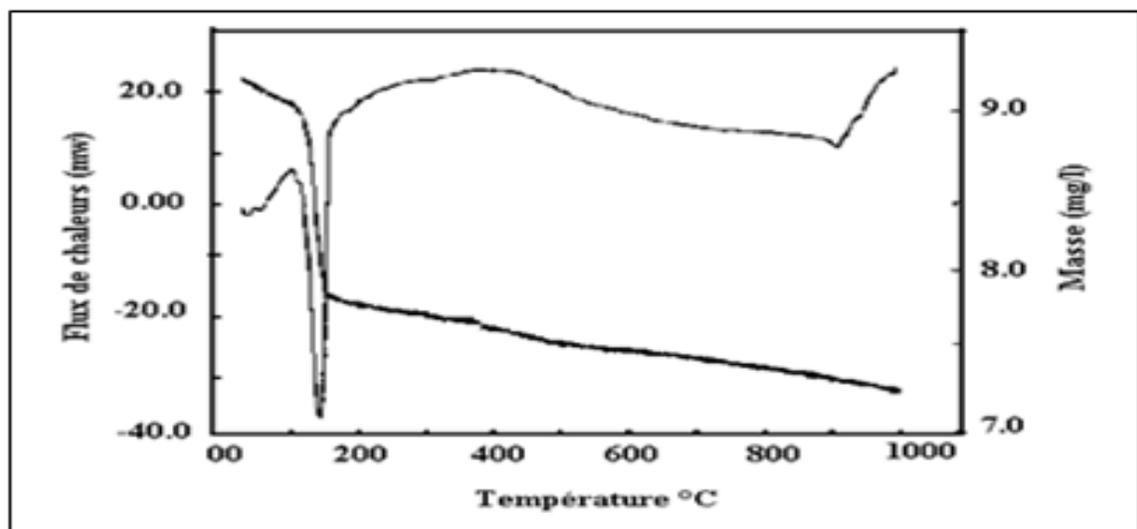
The equilibrium of equation 5 is sensitive to the influence of ions in the liquid phase and to temperature, which tends towards the right side with increasing concentration of H_3PO_4 , H_2SO_4 and

temperature. Consequently, the presence of phosphate compounds in PG, which form H_3PO_4 in the liquid phase, is a possible factor for the appearance of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ in Fig.7b. However, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ crystals are metastable and direct.

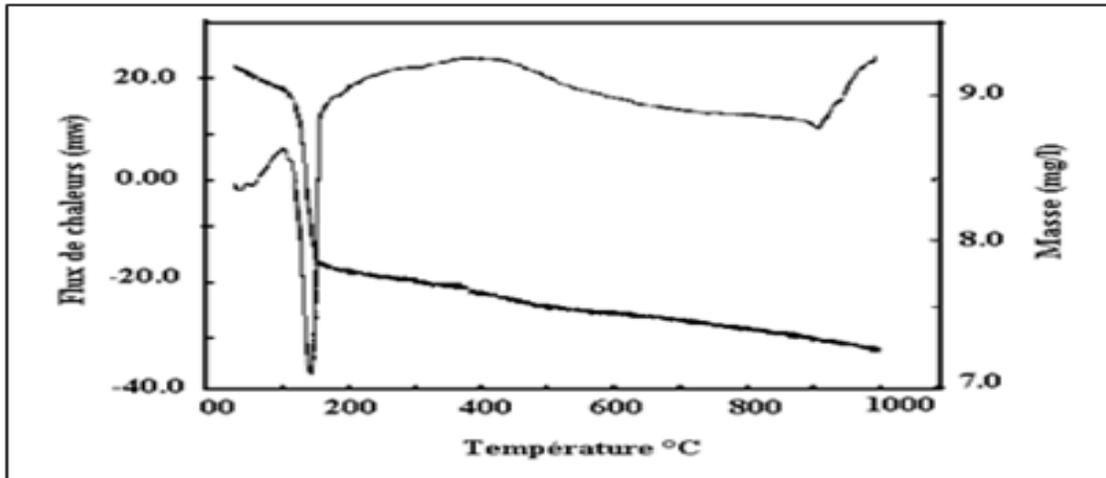
The analyzes carried out on the byproducts of treatment (FTIR, XRD, TGA/TDA) show that they are mostly composed of gypsum: calcium sulphate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). In general, the PG is used in agriculture (for soil stabilization) and construction (preparation of materials for construction / road construction), but in insufficient quantities to absorb all PG generated. The reuse of PG, especially in construction, is based on technical, economic and ecological [40, 41, 42]. In the world, up to 15% of PG produced is used in construction, in general, used in the production of Portland cement [41].



(a)

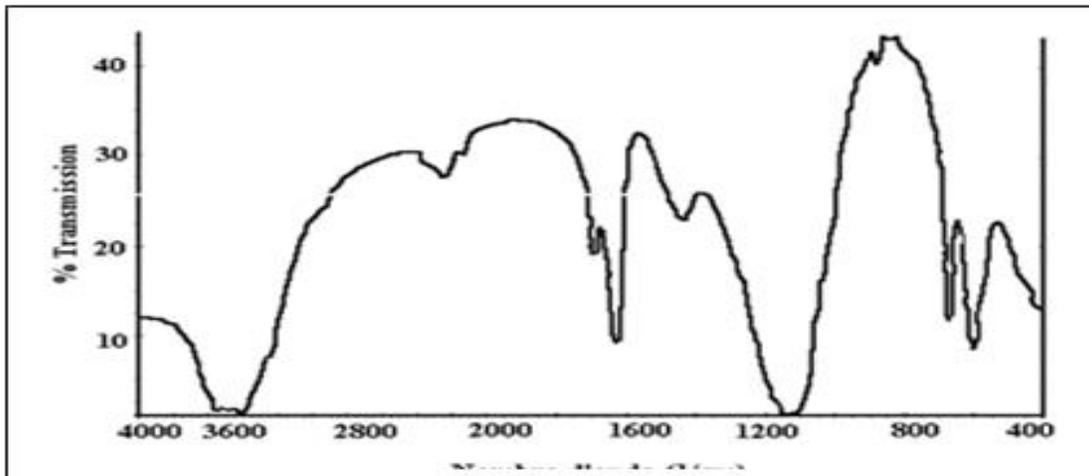


(b)

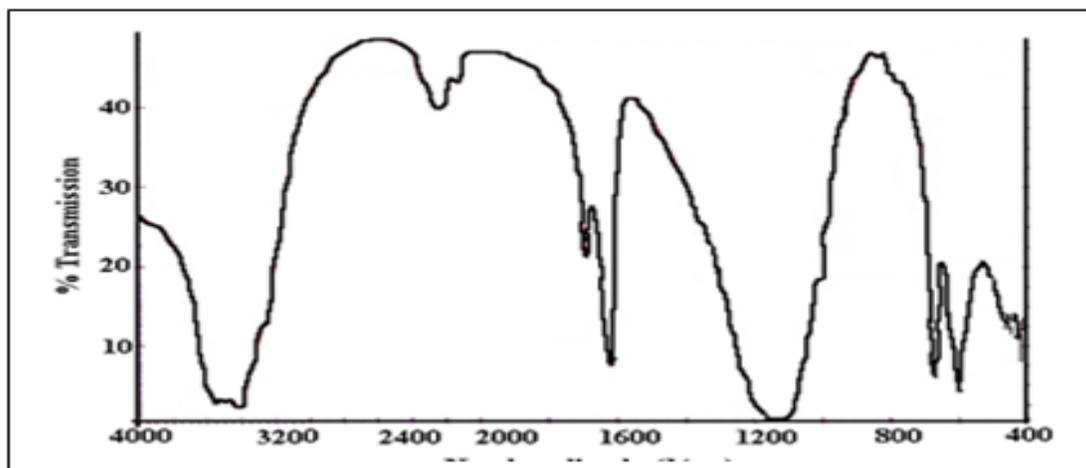


(c)

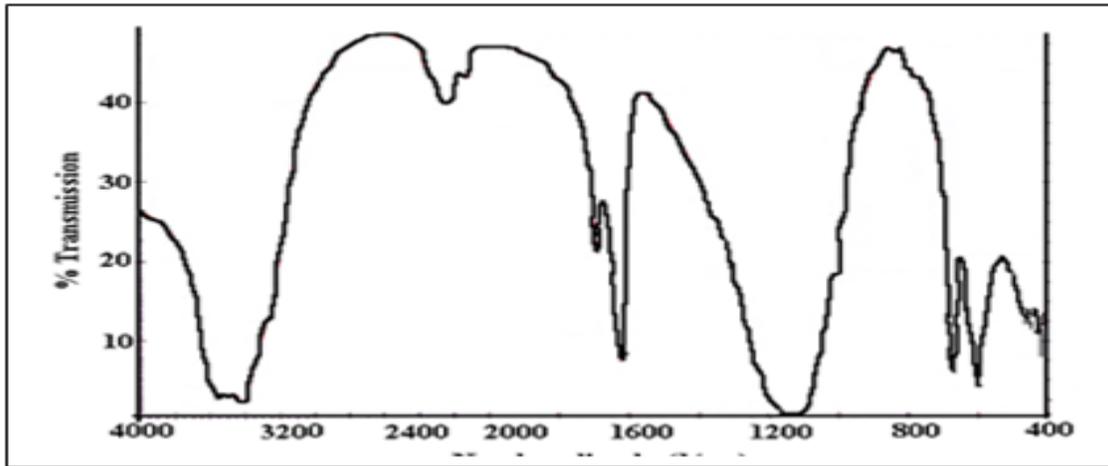
Figure 5: TGA–DTA curves of the byproducts of treatment by (a) lime, (b) limestone and (c) neutralization by NaOH



(a)

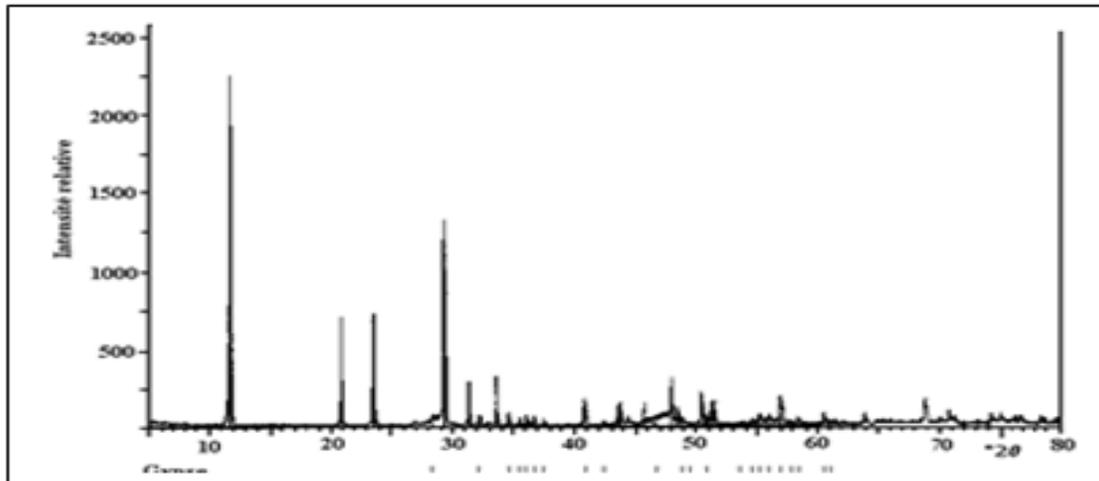


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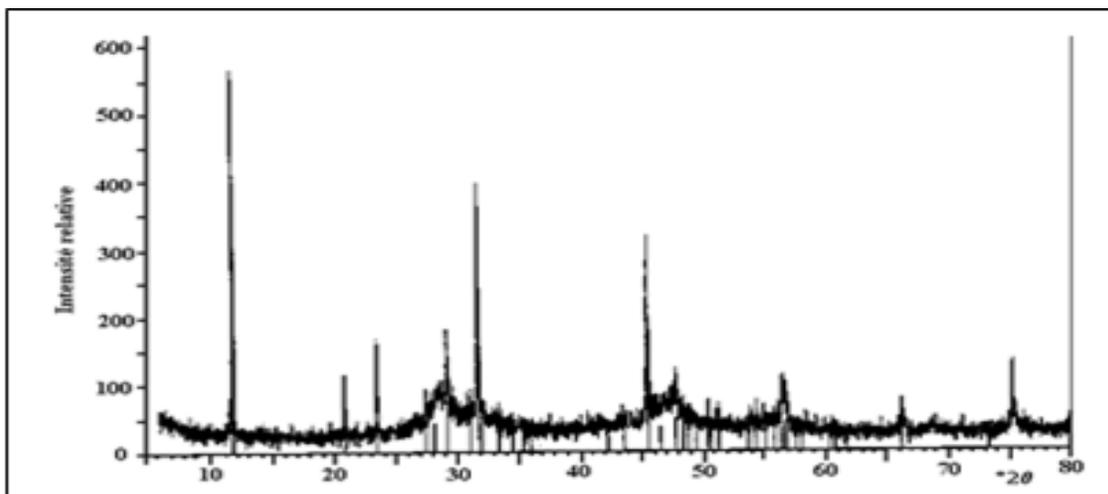


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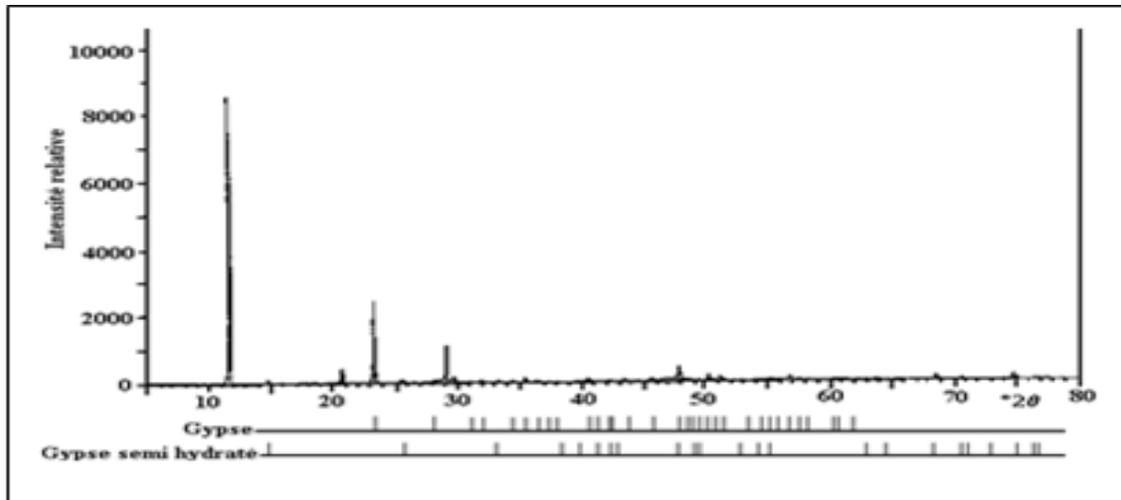
Figure 6: FTIR spectra of the byproducts of treatment by (a) lime, (b) limestone and (c) neutralization by NaOH



(a)



(b)



(c)

Figure 7: XRD patterns of the byproducts of treatment by (a) lime, (b) NaOH and (c) limestone

4. Conclusions

The reduction of pollution due to the discharge industrial rich in heavy metals requires chemical treatment by precipitation for the removal of heavy metals and the recovery of the by-products from this treatment. In this context, a search for the gypsum of these by-products was carried out. The effluent studied is charged in various elements. It is very hard, rich in sulphate, chlorides, orthophosphate and in heavy metals. The method for removing heavy metal from the effluent based on chemical precipitation with lime, limestone and hydroxide sodium has been proposed. The overall results indicate that the optimum pH for hydroxide precipitation of the studied metals is varied between pH 6.0 and 10.0. Since all effluent guidelines require an effluent pH between 7 and 8, the use of carbonate treatment is, therefore, recommended because its buffering capacity value is around pH 7.

The analyzes carried out on the byproducts of treatment show that they are mostly composed of gypsum: calcium sulphate dehydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)

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